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ONR Contract No. Nonr 591-(10)

R. P. I. Project No. 441.35

Technical Report No. 20

December 1963

POTENTIOSTATIC POLARIZATION STUDIES IN FUSED CARBONATES

PART II - STAINLESS STEEL

by

G. J. Janz and A. Conte

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York

To be published in *Electrochim. Acta* - 1964

1964

POTENTIOSTATIC POLARIZATION STUDIES IN FUSED CARBONATES

PART II - STAINLESS STEEL

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G.J. Janz and A. Conte[‡]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N.Y., U.S.A.

ABSTRACT

Electrochemical studies at 600°-700°C are reported for niobium stabilized (347) and χ chromium stabilized (304) stainless steels in the ternary Li_2CO_3 , Na_2CO_3 and K_2CO_3 eutectic mixture by a potentiostatic polarization technique. The results leave little doubt that these stainless steels passivate in fused carbonates. The corrosion potentials for both steels, referred to a Ag/Ag^+ reference half cell, are -525 ± 30 mv (compared to Au and Pt, on the same scale, -470 and -475 mv), and this value is shown to vary qualitatively with environmental effects in accord with the Mass Law controlled equilibrium: $\text{CO}_3^{2-} \rightleftharpoons \text{CO}_2 + \text{O}^{2-}$ in fused carbonates. Values of the primary passive potentials at 600° and 700°C are reported. It is clear that the passivity conferred by anodic electrolysis for these steels makes possible a performance as electrodes quite comparable to that gained when Au-(20%) Pd alloy or Pt are used in the electrolyses of fused carbonates. These properties for stainless steels are discussed relative to current viewpoints on metal passivity, and relative to structural changes found in the steels.

[‡] Post-doctoral Research Fellow, 1962-1963; Present Address: Laboratorio di Chimica delle Radiazioni e Chimica Nucleare, Istituto di Chimica Generale, Citta Universitaria, Roma, Italia.

INTRODUCTION

Information on the properties of stainless steel in contact with fused carbonates at moderately high temperatures (600°-700°C) appears very limited. Chandler and Oser¹ have recently described a study of the electrolytic reduction of carbon dioxide in which the fused carbonate electrolytes were contained in a stainless-steel electrolysis cell, but with no information on the resistivity to chemical attack. Investigations in this laboratory have confirmed² the formation of LiFeO_2 on the surface of stainless steel after immersion in fused carbonates (Li_2CO_3 , Na_2CO_3 , K_2CO_3 eutectic mixture) for prolonged periods at 700°C. A result of this same investigation was a very qualitative indication that a measure of passivity to chemical attack was achieved. Electrochemical studies with the potentiostatic method for further information on the properties of stainless steels in fused carbonates appeared an outstanding need. The present communication reports the results of such an investigation for a niobium stabilized (type 347) stainless steel, for the temperature range 600°-700°C using the ternary Li_2CO_3 , Na_2CO_3 , K_2CO_3 eutectic melt (m.p. 396°C) as electrolyte. Some results for a chromium stabilized (type 304) stainless steel specimen are also reported.

EXPERIMENTAL AND RESULTS

The high temperature experimental cell assembly, reference electrode, auxiliary electrode, potentiostatic circuit, and furnace have been described in detail in the preceding communication³ and were used without modification. The stainless steels (type 304-Fe; 18-20-Cr; 8-11 Ni; 2 max Mn; 0.08 max C; type 347-Fe; 17-19 Cr; 9-12 Ni; Nb, 10X C min; 0.08 max C) were commercially available, and were used in rod form or as tubes for the test electrodes. All measurements were under an atmosphere of carefully dried CO_2 gas, or an equi-molar mixture of CO_2 and O_2 as required for the investigations in progress.

The preparation of the molten carbonate electrolyte was as already described³, and the same care precautions were observed in all the measurements.

The steady state "mixed potentials" or corrosion potentials were first investigated for the test specimens relative to the silver reference electrode standard, using a 5-dial potentiometer and null detector. A period of approximately 24 hours was required to attain the steady-state (equilibrium) values for the stainless steels. A typical "equilibration" period for the Li_2FeO_2 formation on the surface is illustrated in Fig. 1 (347 steel) at 600°C under CO_2 at atmospheric pressure. The values of the corrosion potentials are in Table 1, with the results for the noble metals, Ag, and Ni, listed for comparison.

The corrosion potentials (347 steel) were investigated under varying atmospheres at 600°C . It was noted that if a 1:1 molar mixture of CO_2 and O_2 (total pressure, 1 atm) was bubbled through the fused carbonate, the corrosion potential changed to -450 mv; using N_2 only as the atmosphere, the value changed to -660 mv; with a CO atmosphere, this became to -750 mv. At 700°C , under CO_2 the corrosion potential observed was -720 mv prior to an anodization; after the anodization experiment, this changed to -570 mv.

The potentiostatic polarization properties for the type-347 stainless steel were investigated in the conventional manner⁴. A series of at least four experiments was made for each specimen. Typical results for a series of studies to investigate the influence of various atmospheres and temperature are illustrated in Fig. 2. After each experiment and prior to the next, unless otherwise noted, the specimen was washed with boiling water and dried. The reproducibility of such data was all that could be expected considering the difficulty of such measurements at high temperatures.

The following points are to be noted relative to these experiments (Fig. 2). The passivation loop was not obscured when the anodization was started using a specimen that had not attained the corrosion potential (2-i-a,b) but was obscured when measurements were initiated after the corrosion potential had been attained (2-ii-a). At 700°C, where the corrosion potential was -730 mv, the passivation loop is clearly observed (2-ii-b). The influence of the oxygen content of the atmosphere is strikingly shown in the displacements of the corrosion potentials and of the anodic polarization curves (2-ii-c and d). The results ^A at 700°C, at which temperature a corrosion potential of -720 mv was noted, the anodic polarization curve showed the phenomenon of a cathodic loop; if the electrode was allowed to rest in the melt after this measurement the corrosion potential now noted was -570 mv and subsequent anodization gave the same polarization curve (2-iii-a and b, respectively). This suggests a situation in which the cathodic reduction curve crosses the passivation loop in such a manner that either an active or passive state can be stable^{4a}. Under these circumstances it is possible to break down passivity by application of a suitable cathodic current to the specimen^{5,6}. The anodic polarization curve at 700°C after such a cathodization leaves little doubt that this situation is the one that applies (2-iv). The primary passive potentials found for the niobium stainless steel (type 347) are listed in Table 2.

The possibility that carbon "deposition"³ had occurred during the brief cathodization (2-iv), although in the present work low current densities and short electrolyses times were observed, was considered. To check this factor, a platinum electrode was cathodized at 600°C (0-10 ma, 10 min) and subsequently anodically polarized. It was found as shown in Fig. 3 that the cathodic current decreased smoothly, and that when the applied potential

equalled the corrosion potential of Pt (-475 mv), the sign of the current changed in accord with the observations noted above (Fig. 2-iv). This is strong ^{For the viewpoint} support that the anodic and cathodic loops are not due to carbon "deposition" but relate to primary passivation phenomenon on the surface of the stainless steel.

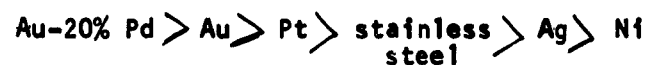
Although type 347 stainless steel is niobium stabilized, prolonged exposures at high temperatures in molten carbonates may be expected to lead to structural changes, and hence to fluctuations in the values of the passive potential, and to the shape of the anodic polarization curve. Several samples, accordingly, were exposed under CO atmospheres at 700°C in contact with molten carbonates for relatively long periods (6 hrs) prior to the anodic polarization measurements. The anodic polarization curve thus gained differed markedly from those previously noted. In Fig. 4 is shown a comparison of such results (^b) with those gained in the manner already described (^a). The difference in results cannot be entirely ascribed to structural changes of the sample since the basicity of the molten electrolyte was undoubtedly increased in the preliminary period of CO treatment.

A limited series of measurements were undertaken with a chromium stabilized stainless steel (type 304). The corrosion potentials at 600° and 700°C were, respectively, -510 and -560 mv (i.e. comparing closely to the values for the 347 stainless steel). The anodic polarization curves for these two types of steels at these two temperatures are shown in Fig. 5.

DISCUSSION

Inspection of the corrosion potentials ~~values~~ (Table 1), shows that the two stainless steels are considerably less reactive than either Ni and Ag at 600°C in molten carbonates, and surprisingly close to the noble metals

in ability to withstand chemical attack. The order in decreasing "nobility" for the metals studied is in the series:



It is also apparent that the displacement of the corrosion potential for stainless steel is in accord with the Mass Law controlled equilibrium in molten carbonates, i.e.:



where the oxygen ion activity, $a_{\text{O}^{2-}}$, is given by $K(\frac{a_{\text{CO}_3^{2-}}}{p_{\text{CO}_2}})$. The oxygen ion activity would be increased in an "inert" atmosphere over the fused carbonates (the system becomes more basic); with either N_2 or CO as the atmospheres, the corrosion potentials were displaced to less noble values (-660 and -750 mv, respectively). When an O_2 - CO_2 gas mixture was used, the corrosion potential was displaced to more noble values (e.g. -450 mv) as would be predicted for Mass Law control in the CO_3^{2-} - CO_2 - O^{2-} equilibrium of fused carbonates.

The potentiostatic polarization results leave little doubt that both type 347 and 304 stainless steels passivate in fused carbonates. The actual properties observed are understood in large part by a model system in which the cathodic reduction curve intersects the anodic loop in a manner to permit either the passive or active states to be stable. This situation is illustrated by the cathodic reduction curve A in Fig. 6a. Whether the active or passive state will be stable is known to depend on accidental factors^{4b}; such behaviour was observed in the present studies (Fig. 2-ii and iii). The fact that the cathodic loop (Fig. 2-ii-b) was not observed at times may be attributed to irreproducible variations in the concentrations of the oxidizing agent in the electrolyte system; this would correspond to a displacement of the cathodic reduction loop as illustrated in Fig. 6a,^D. The case where

spontaneous passivation may be expected at 600°C is illustrated in Fig. 6b for curve T_A . Should the increase in temperature (to 700°C) displace this curve to T_B , it is clear that two corrosion potentials would be possible at the higher temperature, with either the active or passive state being stable. The present results (Fig. 2-iv) confirm that it is possible to break down passivity at 700°C by applying a suitable cathodic current, in accord with the forecast based on the model advanced above (Fig. 6b).

Microscopic examination of both the 347 and 304 stainless steels before and after molten carbonate anodization were undertaken. In Fig. 7 are illustrated the results thus gained for those specimens after electrolyses. The view of the 347 steel (Fig. 7a) shows a cross section of a rod after immersion in the fused carbonate electrolyte for 110 hrs (CO_2 atmosphere); this sample has been used repeatedly for some seven anodic polarization experiments^{at 670°C}. The cross-section for the type 304 steel (Fig. 7b) was from a sample after 20 hrs immersion in the fused carbonates at 625°C, and anodized twice. The microphotographs of these steels before the experiments showed the typical structures of the virgin steels. Inspection of the samples after use in these experiments shows that carbide formation is pronounced in each specimen, but whereas in the niobium stabilized stainless steel this is finely dispersed, in the chromium stabilized specimen, carbide formation is largely localized at the grain boundaries of the steel structure. The external layer^o in the surfaces ~~has been~~^{was} confirmed ~~as~~^{to be} $LiFeO_2$ (~~in a~~^{See} preceding communication² of this series).

The properties of stainless steel in contact with molten carbonates, in comparison with the noble metals and silver, are summarized in Fig. 8 where both the corrosion potentials and potentiostatic anodic polarization curves are illustrated at 600°C. It is clear that with the passivity conferred by anodic electrolysis, the niobium stainless steel (347) ^mcompares closely in

performance to that gained when Au-20% Pd alloy or Pt are used as electrode materials in fused carbonates.

ACKNOWLEDGMENTS

Helpful discussions and continued interest of Dr. N.D. Greene, Electrochemical Laboratory, Rensselaer Polytechnic Institute, are gratefully acknowledged. This work was made possible, in large part, by financial support received from the U.S. Navy, Office of Naval Research, Division of Chemistry, Washington, D.C.

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Table Caption Sheet

Table 1: Corrosion Potentials in Fused Alkali Carbonates at 600°C

Table 2: Primary Passive Potentials for 347 Stainless Steel in Fused Alkali Carbonates

Table 1

Corrosion Potentials in Molten Alkali Carbonates at 600°C

<u>Electrode material</u>	<u>Potential (mv)</u> ***
Au-Pd *	-430
Au *	-470
Pt *	-475
347 ss, 304 ss	-525 ± (30 mv) **
Ag *	-680
Ni *	-1166

*** Gas bubbling through the melt; dry CO₂; all potentials relative to the Ag/Ag⁺ reference electrode.

** average for all experiments.

*see ref. 3

Table 2
Primary Passive Potentials for Type 347 Stainless Steel
in Molten Alkali Carbonates

Temperature (°C)	Potential (mv)	Remarks
600	-1100, -610	two passive potential were observed for the same anodization (Fig. 2-i)
600	-610	after cathodic polarization
700	-680	no cathodic loop obsv'd (Fig. 2-ii)
700	-710	cathodic loop obsv'd (Fig. 2-iii)
700	-690	after cathodic polari- zation, cathodic loop obsv'd (Fig. 2-iv)

Figure Caption Sheet

Fig. 1: Potential vs. time curve for LiFeO_2 formation on type 347 stainless steel at 600°C

Fig. 2: Anodic potentiostatic polarization curves for type 347 stainless steel in fused carbonates

(i) specimen as (a) tube and (b) rod, both not equilibrated to corrosion potential (600°C, CO_2 atm).

(ii) specimen as tube equilibrated to corrosion potential; experiments in the following order with conditions as specified: (a) 600°C, CO_2 ; (b) 700°C, CO_2 ; (c) 600°C, $\text{CO}_2 + \text{O}_2$; (d) 600°C, CO; (corrosion potentials marked on left-hand ordinate axis)

(iii) specimen as tube, equilibrated at corrosion potential; (a) a corrosion potential of -720 mv was initially established (700°C, CO_2), (b) experiment repeated (700°C, CO_2) with same specimen immediately after the preceding was completed.

(iv) The specimen (tube) was cathodized (8 min, 8 ma) prior to this anodic polarization curve (700°C, CO_2)

Fig. 3: Anodic polarization of Pt at 600°C in CO_2 atmospheres

The platinum electrode was previously cathodized (10 min, 0-10 ma); the dotted line illustrates the cathodic current).

Fig. 4: Anodic polarization results for stainless steel at 600°C under CO_2 atmospheres

- (a) sample previously exposed at 700°C for 6 hr. in CO atmosphere
- (b) sample equilibrated at corrosion potential (600°C, CO_2 atmosphere)

Fig. 5: Anodic polarization results for types 304 and 347 stainless steels at 600° and 700°C in CO_2 atmospheres

- (a, b) -304 stainless steel
- (c, d) -347 stainless steel

Fig. 6: Theoretical anodic polarization curves for an active-passive metal

(a) variations in the concentrations of some oxidizing agent may lead to displacements of the cathodic reduction curve (e.g. A and B)

(b) the possible effect of a change in temperature on the passive state is illustrated

Fig. 7: Micro-photographs of the niobium stabilized stainless steel (347) and chromium stabilized stainless steel (304) after prolonged immersion in molten carbonates at 600-700°C

- (a) type 347 steel; 110 hrs, 670°C, 7 anodizations (x 400)
- (b) type 304 steel; 20 hrs, 625°C, 2 anodizations (x 400)

Fig. 8: Comparison of corrosion potential and anodic polarization data for stainless steel (347) a series of metals

(^c~~A~~, 347 stainless steel; ^a~~⌘~~, Pt; ^b~~⌘~~, Au-20% Pd; ^d~~⌘~~, ^{Au}~~Pt~~; ^e~~⌘~~, Ag)

Fig. 1

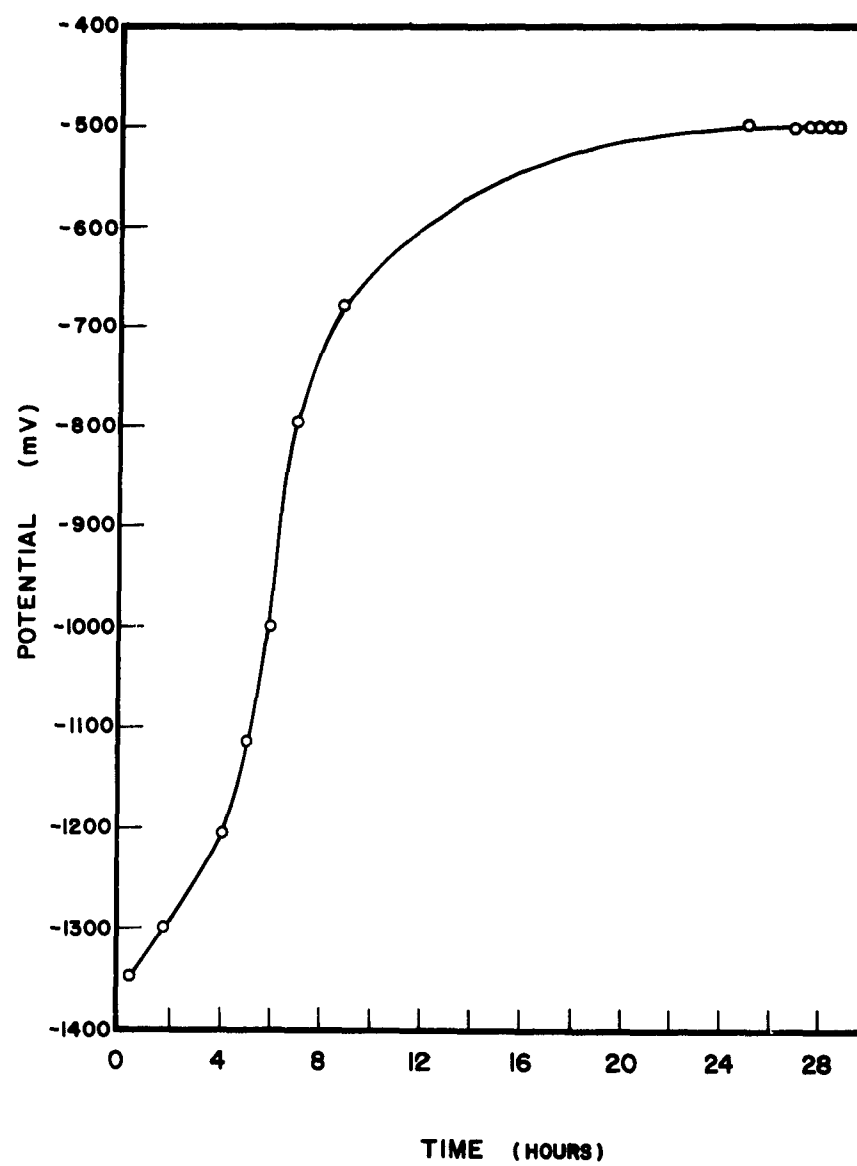


Fig. 2

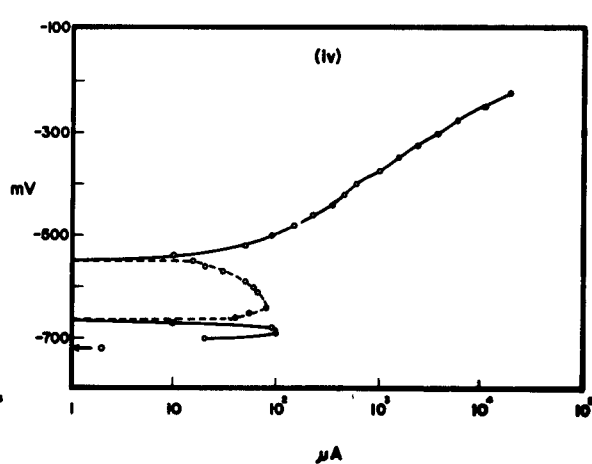
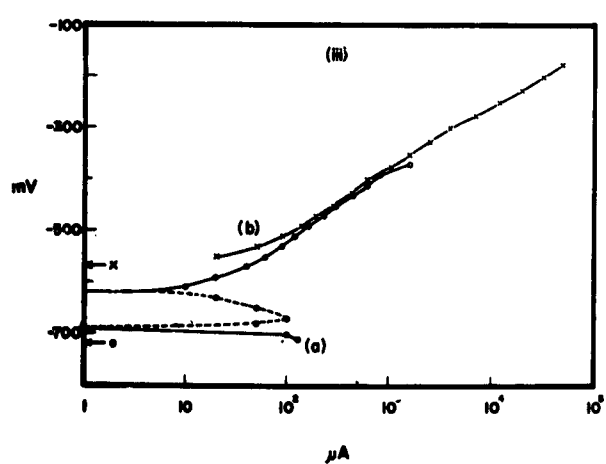
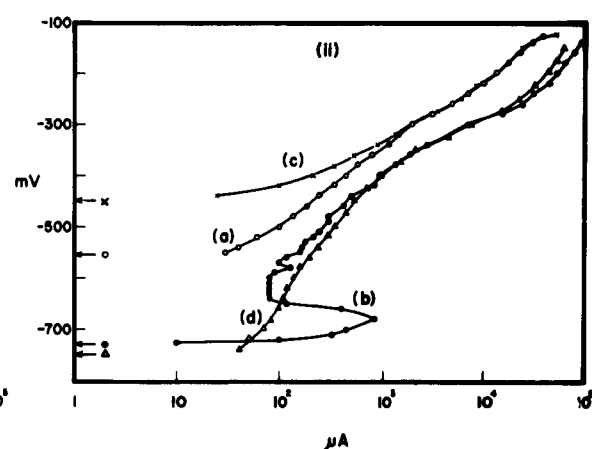
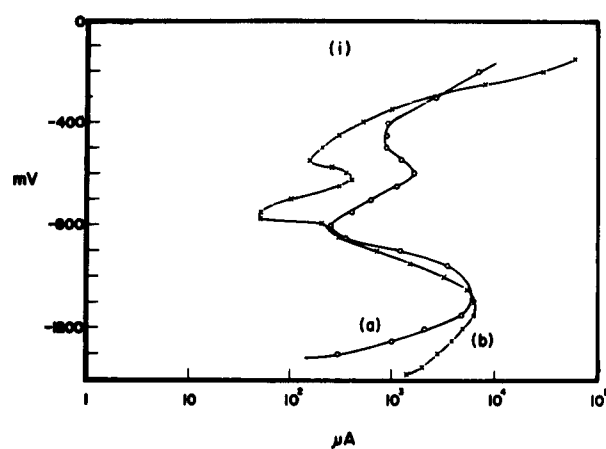


Fig. 3

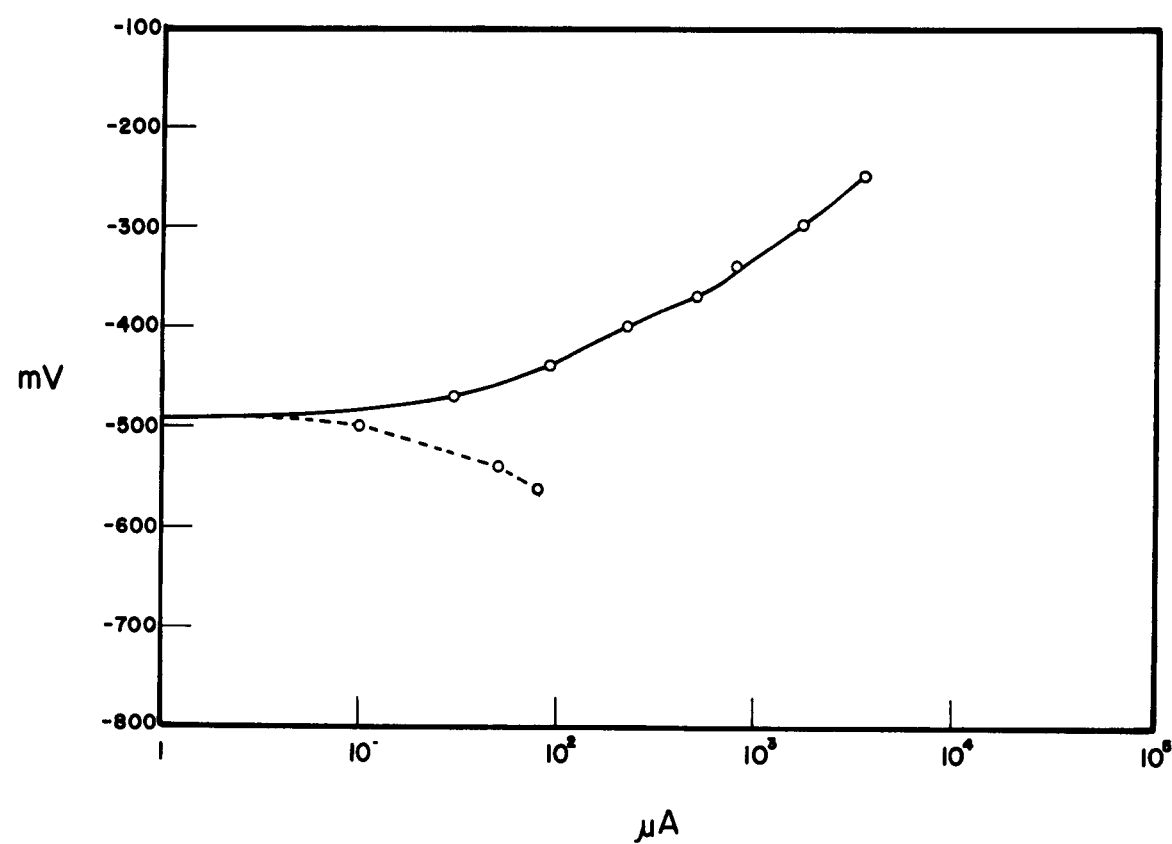


Fig. 4

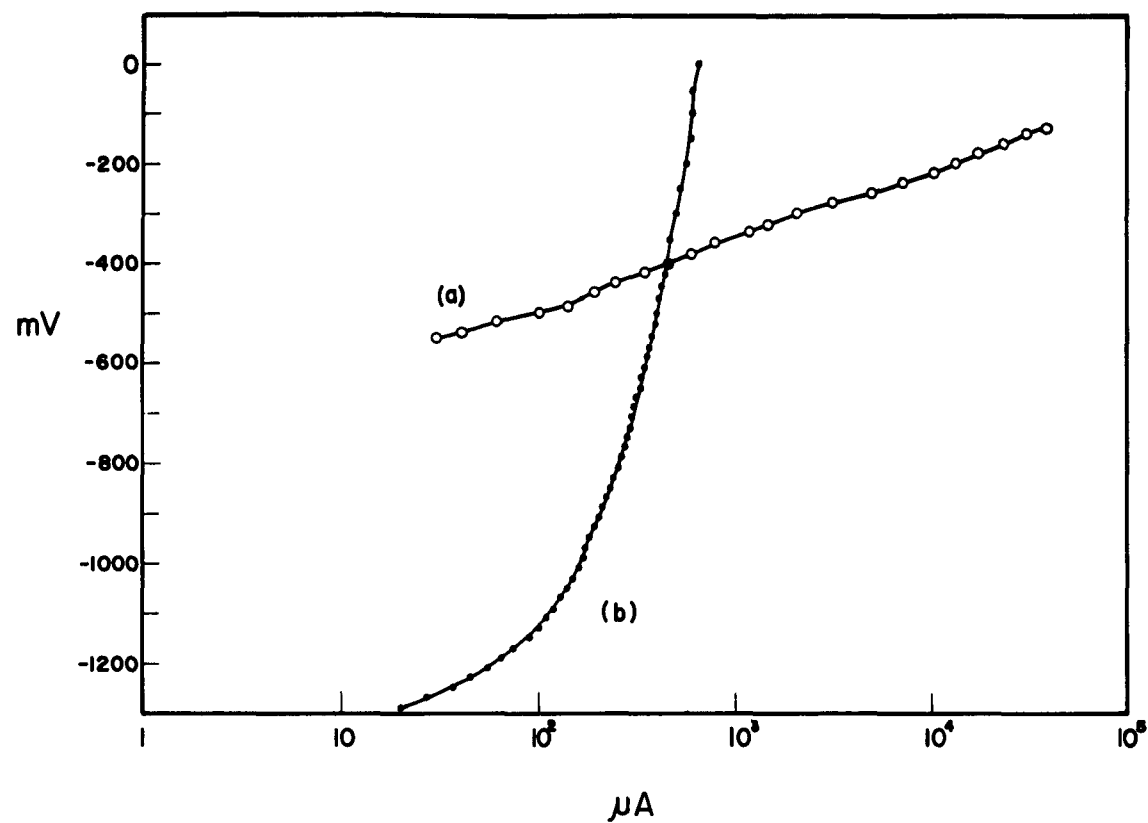


Fig. 5

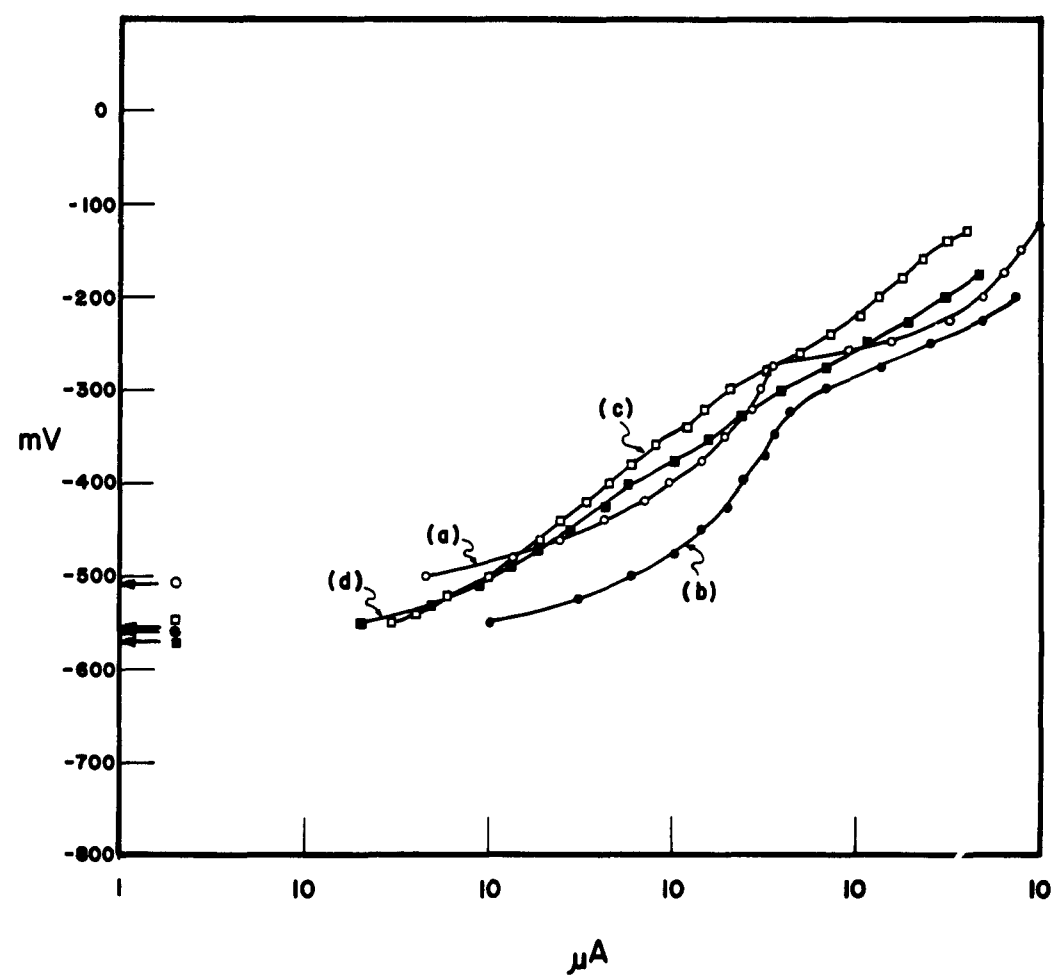
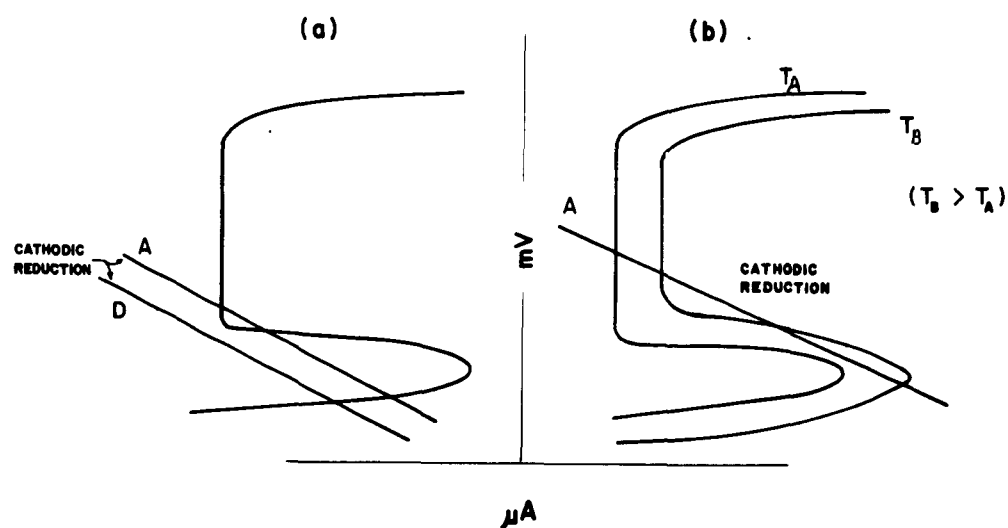
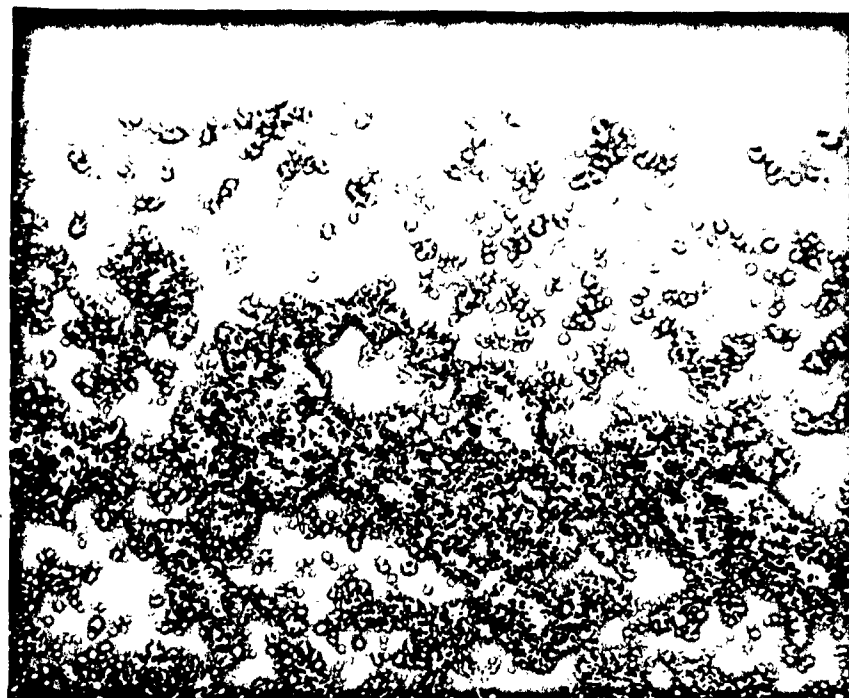
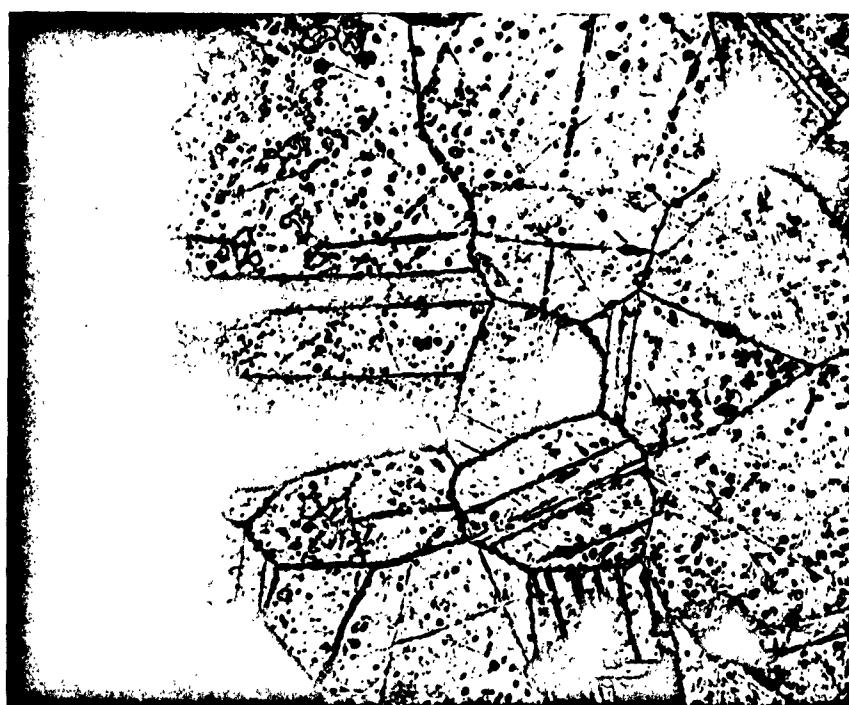


Fig. 6



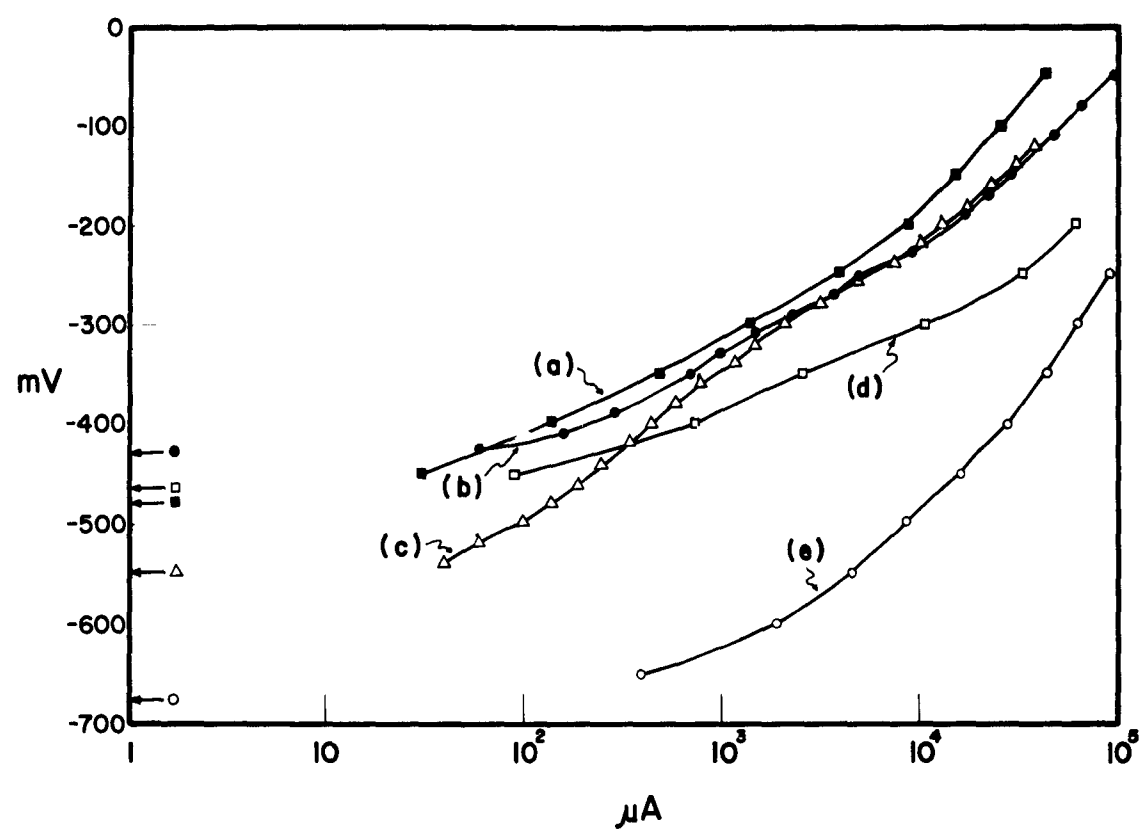


7 a



7 b

Fig. 8



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